PATENT SPECIFICATION

NO DRAWINGS

1,196,087

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Date of Application (No. 14791/68) and filing Complete Specification: 27 March, 1968.

Application made in Canada (No. 988,260) on 19 April, 1967.

Complete Specification Published: 24 June, 1970.

Index at acceptance:—C3 P(2C5, 2C6B, 2C13A, 2C13B, 2C14B, 2D1A, 2D1B, 2D8, 2K7, 2K8, 2S3, 7C5, 7C6B, 7C13A, 7C13B, 7C14B, 7D1B, 7D2A2B, 7D3, 7D8, 7S3)

International Classification:—C 08 d 9/00; C 08 f 41/10

COMPLETE SPECIFICATION

Adhesive Composition

We, POLYMER CORPORATION LIMITED, a company organised under the laws of Canada, of Sarnia, Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to adhesive compositions and, in particular, to adhesive cements containing cross-linked polymer of isobutylene and to a process for their preparation.

It is already known to use a polymer of isobutylene such as butyl rubber in the preparation of adhesive cements. The butyl rubber is a hydrocarbon soluble polymer which, when dissolved, produces an adhesive cement that is difficult to apply using conventional methods because of intensive fibrillation.

It is an object of this invention to provide an improved adhesive composition. Another object is to provide a process of preparing such improved adhesive composition.

It has now ben found possible to prepare an improved adhesive composition using a cross-linked polymer of isobutylene in combination with a soluble elastomer such as butadiene-styrene copolymer. The cross-linked polymer of isobutylene contains at least about 20 per cent by weight of gel and disperses in organic solvents such as toluene to produce a dispersion which is free of coarse gel particles; this dispersion can be sprayed without fibrillation using commercial spray applicators.

In accordance with the present invention, an adhesive composition is provided comprising a dispersion in a volatile organic liquid, i.e. one which boils at a temperature below 150° C. at atmospheric pressure, of a mixture comprising a cross-linked polymer of isobutylene as hereinafter defined, an elastomer as hereinafter defined and a tackifying resin, said polymer of isobutylene containing at least 20 per cent by weight of gel. The invention also provides a process of preparing an adhesive composition which comprises masticating a cross-linked polymer of isobutylene as hereinafter defined containing at least 20 per cent by weight of gel, dispersing said masticated polymer in a volatile organic liquid as defined above to produce a dispersion and incorporating in said dispersion an elastomer as hereinafter defined and a tackifying resin.

The term cross-linked polymer of isobutylene, used in this specification, is applied to copolymers of isobutylene and a small amount of a cross-linking monomer containing at least two independently polymerizable vinylidene groups. These copolymers are characterized by a gel content of at least 20 per cent by weight, preferably 50 to 90 per cent. Gel is determined by dispersing a few grams of the cross-linked polymer in about 100 milliliters of an organic solvent such as toluene, separating the dispersion into a gel phase and a solution, and then determining the amount of polymer present in the solution. The gel content is then calculated from the difference between the amount of polymer used in the dispersion and the amount determined in the solution and is expressed as per cent by weight of the cross-linked polymer of isobutylene. Representative examples of cross-linking monomers are ortho-, meta-, and para-divinyl benzenes, trivinyl benzenes, diallyl benzenes, p- allyl styrene, 2,4-dimethyl pentadiene-1,4 and mixtures thereof. Other non-conjugated multiolefins can also be used. However, it is preferred to use an aromatic hydrocarbon having two vinyl groups attached to aromatic ring. The amount of the cross-linking monomer in the copolymer may vary from 0.1 to 5 mole per cent, preferably from 0.3 to 3.0 mole per cent. The preferred copolymers of isobutylene also contain units of copolymerized conjugated diolefins such as butadiene or isoprene. These units, present in a minor proportion, e.g. less than 10 mole per

[*Price 5s. 0d.*]

cent, provide the cross-linked copolymer with olefinic unsaturation which, if desired, can be used for further cross-linking.

The cross-linked polymer of isobutylene is known in the art and can be used in the form as produced in the polymerization process. However, it is preferred to masticate the polymer to make it uniformly dispersable in a volatile organic liquid and its dispersion in a solvent free of coarse particles and passable through the nozzle of spray applicator. The mastication may be carried out on a rubber mill or in a Banbury mixer at temperatures below 120° C. The time of milling or masticating depends on the type and size of the equipment used, and the uniformity desired in the polymer; as little as three minutes is sufficient for some applications, while in others, carried out under more stringent conditions, milling time of 5—60 minutes is preferred.

The above polymer of isobutylene is dispersed in a volatile organic liquid which boils at temperatures below 150° C. at atmospheric pressure. Representative examples of the organic liquid are aromatic hydrocarbons such as benzene, toluene, xylenes; chlorinated hydrocarbons such as tetrachloroethane, ethylene dichloride, ethyl chloride; aliphatic hydrocarbons such as hexene, isooctane, cyclohexane; ketones such as methyl ethyl ketone; or mixtures thereof. The organic liquid is selected with a view for the specific use; for example a low boiling liquid is used when it is desired to effect a rapid drying of the composition. If, on the other hand, a viscous composition is desired, the organic liquid must be a good solvent for the soluble ingredients of the composition. The organic liquid is preferably used in amounts of not less than 80 per cent by weight of the total composition. The most preferable amount is about 95 per cent by weight.

The composition of this invention also contains an elastomer and a tackifying resin. The elastomer is a high molecular weight non-resinous polymer of a conjugated diolefin, practically all soluble in the organic liquid. It may be a homopolymer of butadiene, isoprene or chloroprene or a copolymer of any of these diolefins with a minor amount of a copolymerizable monoolefinic compound such as styrene, acrylonitrile or vinyl pyridine. The preferred elastomer, however, is a butadiene-styrene copolymer, preferably containing about 20—35 per cent by weight of styrene and having a Mooney viscosity (M/L 4′ @ 100° C.) of about 40 to 60. The relative amount of the preferred elastomer may be varied within wide limits, from $\frac{1}{3}$ part by weight to not more than 5 parts by weight, per 1 part of the cross-linked polymer of isobutylene. When other than the preferred elastomer is used, the relative amount of the elastomer should not exceed about 2 parts by weight per 1 part of the cross-linked polymer.

The tackifying resin may be selected from a variety of soluble resin materials which are compatible, that is, miscible in all proportions with the cross-linked polymer of isobutylene. Representative examples of such resins are phenol-formaldehyde resins, coumarone-indene resins, terpene-phenolic resins, natural wood rosin or modified wood rosins such as polymerized wood rosin or glycerol rosin ester. The selection of a particular resin depends on the substrate to which the composition of this invention is applied and on the strength and/or flexibility of the adhesive bond desired. The proportion of the resin to the cross-linked polymer of isobutylene is normally from 0.25:1 to about 10:1, on a weight basis. The preferable proportion is from 0.5:1 to 5:1.

The components of the adhesive composition of this invention may be mixed in any order as desired. However, it is preferred to disperse the cross-linked polymer of isobutylene in a part or total amount of the organic liquid. Any incompletely dispersed particles may be removed by filtering through e.g. glass wool. The elastomer and tackifying resin may be then incorporated in the solid form and dissolved in the dispersion of the cross-linked polymer; alternatively, they may be dissolved in a part of the organic liquid prior to adding to the dispersion and then the solution thereof mixed with the dispersion to produce the adhesive composition of this invention.

The invention is further illustrated by means of the following examples.

Example I.

An adhesive composition was prepared from a cross-linked polymer of isobutylene having a Mooney viscosity (M/L 9′ @ 125° C.) of 55, measured at 125° C. after 9 minutes of rotation using large rotor, and a gel content of 20 per cent by weight. For the determination of gel, the polymer was suspended in cyclohexane, agitated at 20° C. for 48 hours and then the dispersion was filtered through a #541 "Whatman" filter paper ("Whatman" is a Trade Mark). The amount of gel was calculated from the concentration of the polymer in the filtrate. This polymer of isobutylene was a copolymer prepared by copolymerizing at about −100° C. in methyl chloride diluent and in the presence of $AlCl_3$ catalyst a monomer mixture consisting of 100 parts by weight of isobutylene, 3 parts by weight of isoprene and 3 parts by weight of divinyl benzene. Prior to dispersing, the polymer was milled for 40 minutes at room temperature on a laboratory two roll mill at a setting of the gap between the rolls of about 0.5 mm.

25 grams of the above polymer was added to 810 grams of toluene and agitated at room temperature until a uniform dispersion was obtained. To this dispersion there was gradually added and dissolved 47 grams of a butadiene-

styrene copolymer, 94 grams of wood rosin and 2 grams of 2,2 - methylene bis - (4 - methyl - 6 - tertiary butyl phenol), the antioxidant. The butadiene-styrene copolymer was a hot emulsion-polymerized, essentially all soluble, polymer containing 28 per cent by weight of styrene and having a Mooney viscosity (M/L 4′ @ 100° C.) of 47. A smooth, uniform and fluid composition was obtained. This composition was sprayed onto a cotton duck fabric of 5 centimeters width, using a laboratory atomizer. The spray operation was smooth and free of fibrillation. After the toluene had evaporated, the cotton duck strips were bonded under pressure and then tested for peel strength. A force of 16.3 kilograms was required to peel off the strips.

A control experiment was carried out with an adhesive composition as above except for the omission of the cross-linked polymer of isobutylene. Severe fibrillation was observed when this composition was sprayed using the same laboratory atomizer.

EXAMPLE II.

Four adhesive cements were prepared according to the procedure of Example I. These cements contained, dispersed in toluene, 3 per cent by weight of non-volatile components shown in the following table. The amounts in the table are parts by weight per 100 parts of the cross-linked isobutylene polymer.

TABLE

Composition	1	2	3	4
Cross-linked isobutylene polymer	100	100	100	100
Butadiene-styrene copolymer	300	300	300	300
Antioxidant	4	4	4	4
Wood rosin	—	—	—	140
Alkyl-phenol formaldehyde resin	140	280	140	—

The cross-linked isobutylene polymer, used in this example, was a copolymer of isobutylene, isoprene, and divinyl benzene containing 70 per cent of gel. It was milled at room temperature for 10 minutes (compositions 1 and 2) and 60 minutes (compositions 3 and 4), respectively. The butadiene-styrene copolymer, antioxidant and wood rosin all were the same as in Example I. The alkyl-phenol formaldehyde resin was a heat-reactive resin having a melting point range of 144—162° available from Schenectady Chemicals, Inc., under the trade name SP—103 Resin.

All the cements were low viscosity dispersions which, when atomized, formed a spray practically free of fibrils. Compositions 3 and 4 were more uniform than compositions 1 and 2.

Additional cements were made using composition 4 in which the butadiene-styrene copolymer was replaced by the same amount of a butyl rubber and a butadiene-acrylonitrile copolymer, respectively. The butyl rubber was completely soluble in toluene and had a Mooney viscosity (M/L 8′ @ 100° C.) of 45 and the butadiene-acrylonitrile copolymer had an acrylonitrile content of 34 per cent by weight and a Mooney viscosity (M/L 4′ @ 100° C.) of 83. These cements were fluid and uniform dispersions, but could not be sprayed without fibrillation.

WHAT WE CLAIM IS:—

1. An adhesive composition comprising a dispersion in an organic liquid which boils at a temperature below 150° C. at atmospheric pressure of a mixture comprising a cross-linked polymer of isobutylene as hereinbefore defined, an elastomer as hereinbefore defined and a tackifying resin, said cross-linked polymer containing at least 20 per cent by weight of gel.

2. The composition of Claim 1 in which the cross-linking monomer is divinyl benzene.

3. The composition of Claim 1 in which the cross-linked polymer of isobutylene is a copolymer of isobutylene, a minor proportion of isoprene and a small amount of a cross-linking monomer containing at least two independently polymerizable vinylidene groups.

4. The composition of any of Claims 1—3 in which the organic liquid is present in an amount of not less than 80 per cent by weight of the composition.

5. The composition of any of Claims 1—4 in which the proportion of the tackifying resin to the cross-linked polymer of isobutylene is from 0.25:1 to 10:1 on a weight basis.

6. The composition of any of Claims 1—5 in which the elastomer is a butadiene-styrene copolymer.

7. An adhesive composition comprising a dispersion in not less than 80 parts by weight

of an organic liquid which boils at a temperature below 150° C. at atmospheric pressure of not more than 20 parts by weight of a mixture of (1) a cross-linked copolymer of isobutylene, isoprene and divinyl benzene, said cross-linked copolymer (1) containing less than 10 mole per cent of isoprene units and from 0.1 to 5 mole per cent of divinyl benzene units and at least 20 per cent by weight of gel, (2) a butadiene-styrene copolymer and (3) a tackifying resin, the proportion of said resin (3) to said cross-linked copolymer (1) being from 0.25:1 to 10:1 on a weight basis.

8. The composition of Claim 6 or Claim 7 in which the amount of the butadiene-styrene copolymer (2) is from ¼ part to not more than 5 parts by weight per 1 part of the cross-linked copolymer (1).

9. The composition of any of Claims 1—8 wherein the cross-linked isobutylene polymer contains 50 to 90 per cent gel.

10. A process of preparing an adhesive composition which comprises masticating a cross-linked polymer of isobutylene as hereinbefore defined containing at least 20 per cent by weight of gel, dispersing said masticated polymer in an organic liquid which boils at a temperature below 150° C. at atmospheric pressure to produce a dispersion and incorporating in said dispersion an elastomer as hereinbefore defined and a tackifying resin.

11. The process according to Claim 10 in which the cross-linked polymer is a copolymer of isobutylene, isoprene and divinyl benzene, said copolymer containing less than 10 mole per cent of isoprene units and from 0.1 to 5 mole per cent of divinyl benzene units.

12. The process according to Claim 10 in which the elastomer is a butadiene-styrene copolymer.

13. The process according to any of Claims 10, 11 or 12 in which the cross-linked polymer of isobutylene is masticated at a temperature below 120° C.

14. The process according to any of Claims 10—13 in which the cross-linked polymer is masticated for at least 3 minutes.

15. A composition substantially as hereinbefore described with reference to the foregoing Examples.

16. A process substantially as hereinbefore described with reference to the foregoing Examples.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.